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(54) **Rigid resin composition having electromagnetic shielding properties.**

(57) A hybrid resin composition superior in electromagnetic shielding property, rigidity and mouldability is obtained by mixing (A) 10 to 50 parts by weight of electrically conductive inorganic powdery or granular substances, which are obtained by coating the surface of flaky nonmetallic inorganic powdery or granular substances with electrically conductive materials having volume resistivity of 1 ohm·cm or less; (B) 1 to 20 parts by weight of an electrically conductive fibrous substance and/or electrically conductive corpuscles having a volume resistivity of 1 ohm·cm or less, and (C) 30 to 80 parts by weight of a resin.

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RIGID RESIN COMPOSITION HAVING ELECTROMAGNETIC SHIELDING PROPERTIES

The present invention relates to hybrid resins having electromagnetic shielding properties.

Recently, the problem of electromagnetic interference has intensified with progress in electronic equipment. Electromagnetic interference can cause such troubles as malfunctioning of computers, owing to various kinds of noise under various kinds of environment. This can lead to serious accidents since many more types of apparatus are now controlled by computers than hitherto. Moreover, housings for apparatus are usually made of plastics materials in order to obtain lightweight and compact apparatus and instruments. In the United States of America, regulations such as those by the Federal Communications Commission have been established. There are three countermeasures against "electromagnetic interference" at present: (1) metal spraying, (2) electrically conductive coatings and (3) electrically conductive filler-filled plastics. Countermeasures (1) and (2) are expensive and short-lived. Recently, the technical field of (3) has been investigated with keenest interest. Although metal fibres and metal flakes, metallic corpuscles and graphite corpuscles are exclusively investigated for such electrically conductive fillers, it is not easy to obtain moulded products from a mixture comprising resin to which large amounts of metal fibres or metal flakes have been added. In addition, it is difficult to achieve the intended performances of moulded products since such fillers are changed in shape in the melt mixing step of injection moulding and extrusion moulding owing to their softness, and thus show uneven distribution in moulded products.

On the other hand, if only a small amount of metal fibres or metal flakes is added, no electromagnetic shielding effect can be achieved. Further, insulation properties are also required since it is extremely dangerous to make electronic equipment electrically conducting when there is a short circuit.

Thus, the seemingly contradictory properties of electrical conductivity and insulation are required. In addition, rigidity and heat

resistance are required for housings of electronic instruments and communications equipment. Materials that can satisfy all of these requirements have not yet been developed. Moreover, the electromagnetic shielding effect has not yet been fully investigated.

Thorough investigations of the materials capable of satisfying the requirements described above showed that a resin composition comprising resin and a definite proportion of electrically conductive filler is superior in electromagnetic shielding property and rigidity. This resin composition is disclosed in Japanese Patent Application No. 197229/1982. The electrically conductive fillers are electrically conductive inorganic powdery or granular substances obtained by coating the surface of flaky non-metallic inorganic powdery or granular substances with electrically conductive substances. More specificially, if the electrically conductive fillers are obtained by coating, with certain electrically conductive substances, the surface of (a) micaceous inorganic powdery or granular substances showing plastic deformation with difficulty and have a flexural modulus of 2×10^6 kg/cm^2 or (b) glass flakes having flexural modulus of 7×10^5 kg/cm^2, and are used as one ingredient of said resin composition, they show substantially no deformation or breakage when incorporated into a resin, they are capable of increasing the rigidity of the resin composition, they do not show uneven distribution in moulded products, and they have a superior electromagnetic shielding effect at a smaller ratio compared with metal fibres or metal flakes. Such a superior electromagnetic shielding effect is perhaps caused by the high rigidity of the flaky nonmetallic inorganic powdery or granular substances used as a base. However, such a treatment for giving electrical conductivity increases the cost and causes deterioration of the mouldability of the resin composition, since the rigidity of the composition is improved in fabrication, e.g. by vacuum-moulding after mixing and extrusion-moulding into sheet-like materials.

Hybrid resin compositions, which can show superior characteristics by using different kinds of additive together, are known. In the field of electromagnetic shielding materials, and electromagnetic shielding material comprising 10 to 25% by volume of electrically conductive short fibres and 2 to 40% by volume of electrically conductive powdery or granular substances is disclosed for example, in Japanese Laid-Open Patent Application No. 56200/1979. In addition, an electrically conductive plastic composition for

electromagnetic shielding comprising 0.2 to 5% by volume of metal fibres and 1 to 10% by volume of metallic powders is disclosed in Japanese Laid-Open Patent Application No. 65754/1982. However, all of such hybrid compositions comprise metals as the fundamental materials and have an effect such that the number of mutual contact points is increased by mixing two kinds of metal of different shapes, whereby electrical conductivity of the resulting composition is increased. However, the metal fibres or flakes are liable to be changed in shape in mixing with resin and moulding, and metal fibres or flakes can become entangled and thus choke a nozzle, thereby causing deterioration in the mouldability of the composition. In addition, metal fibres or metal flakes are liable to be broken or cut if the mixing time is comparatively long or the rate of shear in mixing is large, so that the expected electromagnetic shielding effect sometimes cannot be achieved. The flexural modulus of such metallic fundamental materials is comparatively small, for example 2.6 x 10^5 kg/cm_2 for aluminium alloys and 3.1 x 10^5 kg/cm^2 for copper alloys, which makes them liable to be deformed. Such disadvantages cannot be mitigated even in the above described hybrid composition. Accordingly, hybrid compositions containing electrically conductive metallic fillers have been used merely for manufacturing large-sized products of simple shapes by injection moulding at a comparatively low rate of shear with a large gate.

In accordance with the present invention, a hybrid resin composition comprises (A) 10 to 50 parts by weight of electrically conductive inorganic powdery or granular substances, which are obtained by coating the surface of flaky nonmetallic inorganic powdery or granular substances with electrically conductive materials having volume resistivity of 1 ohm•cm or less; (B) 1 to 20 parts by weight of an electrically conductive fibrous substance and/or electrically conductive corpuscles having a volume resistivity of 1 ohm•cm or less, and (C) 30 to 80 parts by weight of a resin.

In general a filler having lower rigidity and a fibrous filler having a larger aspect ratio are more severely broken and deformed when two kinds of filler having different rigidities and shapes are mixed together. It is expected that metal fibres would also be severely deformed and broken in the case of a hybrid composition comprising electrically conductive inorganic powdery or granular substances obtained as already mentioned and hereinafter referred to as flaky inorganic powdery or granular substances,

together with metal fibres. However, the present inventors unexpectedly found that the deformation and breakage of metal fibres were not appreciable when a hybrid composition comprising such flaky non-metallic inorganic powdery or granular substances, metal fibres and resin was moulded: indeed, the hybrid composition was rather remarkably improved in respect of the breakage and deformation of metal fibres as compared with those of a composition in which metal fibres alone were added to resin. As a result, the present invention was achieved. Although it is difficult to clearly describe the mechanism producing the superior effects of the present invention, the inventors believe it to be as follows.

One of the characteristics of the present invention is in rigidity, elastic deformation properties and shape (flaky) of the flaky inorganic powdery or granular substances. Consequently, the flaky inorganic powdery or granular substances are easily orientated when a resin composition containing such fillers is moulded, e.g. by injection moulding. The orientated flaky inorganic powdery or granular substances can have a reduced contact resistance, whereby the volume resistivity of the moulded products is reduced and their electromagnetic shielding effect can also be increased. In addition, the orientated flaky inorganic powdery or granular substances show protective action for metal fibres, which have lower rigidity and are apt to be subjected to plastic deformation in a hybrid resin composition. Possibly the deformation and breakage of metal fibres during mixing of a composition can be prevented since they flow if they are put among the flaky inorganic powdery or granular substances.

In the accompanying drawings:-

Fig. 1 shows schematically a section through a moulded product obtained from a hybrid resin composition comprising an electrically conductive inorganic powdery or granular substance, an electrically conductive fibrous substance and a resin according to the present invention;

Fig. 2 shows schematically a section through a moulded product obtained from a hybrid resin composition comprising an electrically conductive powdery or granular substance, electrically conductive corpuscles and a resin according to the present invention;

Fig. 3 shows schematically a section through a moulded product obtained from a conventional hybrid resin composition comprising an electrically conductive fibrous substance, metal flakes and a resin;

Fig. 4 is a microphotograph of a moulded product obtained from a hybrid resin composition obtained in Example 4;

Fig. 5 is a microphotograph of a moulded product obtained from the conventional hybrid resin composition obtained in Comparative Example 7; and

Fig. 6 is a microphotograph of a moulded product obtained from the conventional hybrid resin composition obtained in Comparative Example 8.

In Fig. 1, 1 designates flaky electrically conductive nonmetallic inorganic powdery or granular substances, 2 designates electrically conductive fibrous substances, and 4 designates a resin. In addition, when electrically conductive corpuscles are used instead of metal fibres, the deformation and breakage of electrically conductive corpuscles is possibly prevented because the chain cohesion state of the electrically conductive corpuscles formed in the resin remains protected in the mixing and flowing processes, whereby a superior electromagnetic shielding effect is achieved.

Referring now to Fig. 2, which is a sectional view schematically showing the above described state, 3 designates electrically conductive corpuscles. Further, Fig. 3 is a sectional view schematically showing a moulded product of a conventional hybrid composition comprising resin 4, metal flakes 5 and metal fibres 2. However, in this case, the metal flakes and metal fibres are deformed and broken and show the mal-distribution, so that the satisfactory electromagnetic shielding effect cannot be achieved. This hybrid composition is inferior in rigidity and mouldability, too.

The flaky nonmetallic inorganic powdery or granular substances used in the present invention include mica, talc, sericite, glass flake, stratified graphite, vermiculite, bentonite and attapulgite. It is desirable that the flaky nonmetallic inorganic powdery or granular substances have an average diameter of 5 to 3,000 μm and an average aspect ratio of 10 or more in respect of mouldability and physical properties of moulded products. Natural or artificial minerals belonging to the mica group, clintonite group or chlorite group are particularly preferred, and especially natural muscovite, phlogopite, biotite, vermiculite and fluorine mica.

Any electrically conductive substances having volume resistivity of 1 ohm·cm or less can be used for coating the surface of the flaky nonmetallic inorganic powdery or granular substances. Silver, copper, iron, nickel, aluminium, tin, chromium, titanium, zinc, gold or platinum or their alloys or

graphite is preferably used in respect of electrical conductivity, adhesiveness and cost. It is desirable that the surface of the flaky inorganic powdery or granular substances be coated with 0.2 to 1 times its weight of the electrically conductive substances, depending on the mixture ratios of the flaky inorganic powdery or granular substances and the resin in respect to the electromagnetic shielding property. The electromagnetic shielding effect is little when the surface of the flaky inorganic powdery or granular substances is coated with less than 0.2 its weight of the electrically conductive substances, while sometimes resin decomposes or deteriorates at high temperature when the surface of the flaky inorganic powdery or granular substances is coated with more than its own weight of the electrically conductive substances.

Any electroless plating method, e.g. (a) dispersion of the flaky inorganic powdery or granular substances in an aqueous solution of metallic chloride compounds having the suitable concentrations followed by evaporating or otherwise treating the solution to deposit metallic particles on the surface of the flaky inorganic powdery or granular substances, (b) a high-vacuum metallizing method, (c) a sputtering method, or (d) an ion-plating method, can be used for coating the surface. Alternatively the surface can be coated with a layer of a suitable binder and electrically conductive corpuscles stuck to the layer of binder. It is desirable in respect of various kinds of performance that the coated layer of electrically conductive substances be 0.01 μm to 1 mm, preferably 0.05 to 100 μm, thick.

Although any electrically conductive fibroid substances having volume resistivity of 1 ohm•cm or less can be used in the present invention, in general it is desirable that the electrically conductive fibroid substance have an average aspect ratio of 10 or more, an average diameter of 0.1 μm to 3 mm and an average fibre length of 10 μm to 50 mm. Metal fibres, organic or inorganic fibres coated with metal, carbon fibres, graphite fibres, organic fibres containing metallic corpuscles, general antistatic organic fibres, or carbon corpuscles or mixtures consisting of two or more kinds of such fibre are suitably used in respect of electrical conductivity, mouldability and cost. Examples of suitable metallic fibres include short fibres and whiskers of iron, stainless steel, aluminium, nickel, copper, brass, bronze, lead, tungsten and molybdenum, obtained by drawing, a melt-spinning, cutting, shearing or crystallization; examples of organic or

inorganic fibres coated with metal include glass fibres whose surface is plated, coated or high-vacuum metallized with aluminium or nickel; examples of carbon fibres or graphite fibres include fibres obtained from such starting materials as acrylic fibres, rayon, petroleum pitch and coal pitch, and examples of organic fibres containing metallic corpuscles or carbon corpuscles include electrically conductive fibres obtained by dispersing metallic corpuscles such as silver, copper, brass, nickel, aluminium and iron or electrically conductive graphite corpuscles such as acetylene black and ketjenblack in organic fibres having comparatively high melting points such as polyester. In addition, the electrically conductive corpuscles used in the present invention include metallic corpuscles such as silver, copper, brass, nickel, aluminium and iron, and electrically conductive graphite corpuscles such as acetylene black and ketjenblack having an average diameter of 100 μm or less. The electrically conductive fibroid substances and electrically conductive corpuscles used in the present invention couple the flaky electrically conductive inorganic powdery or granular substances, which are the main electrically conductive fillers. The electrically conductive corpuscles form a chain, cohesion structure when dispersed in resin to play the same part as the electrically conductive fibrous substances.

The volume resistivity value, which is frequently used as a physical property for specifying the materials used in the present invention, will be described below. Volume resistivity, which is used as the specifying value of the electrically conductive substances to be coated on the surface of the flaky nonmetallic inorganic powdery or granular substances, for example metals, alloys or graphite, is peculiar to such substances. The usual method for evaluating electrical conductivity of metal plates and metal rods can be used in order to measure volume resistivity. However, volume resistivity used for specifying the properties of the electrically conductive fibrous substances and electrically conductive corpuscles must be not a property peculiar to the materials making up the electrically conductive fibroid substances and electrically conductive corpuscles, but the value for substances of fibroid shape or corpuscular shape. For example, although the fundamental volume resistivity of the materials constructing metal fibres is of the order 10^{-6} to 10^{-5} ohm•cm, the volume resistivity of the products worked into fibroid substances is of the order 10^{-3} to

10^{-2} ohm·cm, as measured by a method described later. In addition, it sometimes surpasses 1 ohm·cm owing inter alia to oxidative damage of the surface of the electrically conductive substances. On the other hand, although glass fibres are insulating materials having a volume resistivity of 10^{10} ohm·cm or more, aluminium-coated glass fibres show volume resistivity of around 10^{-2} ohm·cm, which is within the range usable in the present invention.

Although there is no special method of measuring volume resistivity of fibrous substances or corpuscles, it can be measured by methods that have been used for making such measurements on electrically conductive materials, for example a double bridge method, using a sample obtained by suitably filling an insulating cylindrical receptacle with the fibrous substances or corpuscles. However, in this case, the contact resistance between the electrically conductive fibrous substances or corpuscles is measured: this fluctuates depending on the pressure used for filling the insulating cylindrical receptacle with them. Although, strictly speaking, the measured values ought to be compared at the same volume percent of samples in receptacles, electrical resistivity, if it is 1 ohm·cm or less, can be usually evaluated by measuring at a load of about 50 g/cm^2, since in general volume resistivity slightly fluctuates depending on how the receptacle is filled with the fibrous substances or corpuscles.

The resin used in the present invention may be any mouldable material of high molecular weight. Thermoplastic resins such as polyvinyl chloride, polyethylene, polypropylene, polystyrene, polymethyl methacrylate, AS resin, ABS resin, polyethylene terephthalate, polybutylene terephthalate, polycarbonate resins, polyurethane resins, polyacetal resins, polyimide resins and nylon resins; copolymers of the above; emulsion-type resins of such materials as polyvinyl acetate, vinyl acetate-ethylene copolymer, polyvinyl chloride and polyacrylic acid ester; latex-type resins or bulk rubber of SBR and various kinds of natural and synthetic rubber; and thermosetting resins, such as unsaturated polyester resins, epoxy resins, phenolic resins, urea resins and melamine resins can be used. Fillers such as calcium carbonate, barium sulphate and clay, pigments such as carbon black and titanium dioxide, antioxidants, ultraviolet absorbers, silane coupling agents, internal removers and other additions can be suitably added in accordance with the use desired.

In order to give full play to the effects of the present invention, it is necessary to add the electrically conductive inorganic powdery or granular substances and the electrically conductive fibroid substances and/or corpuscles to the resin in the proportions stated. Electrical resistivity of moulded products is reduced, whereby the electromagnetic shielding effect is reduced, when the electrically conductive inorganic powdery or granular substances or the electrically conductive fibrous substances and/or corpuscles are added in smaller quantities, while it is difficult to mould a hybrid composition and thus obtain products having a beautiful appearance when the amount of electrically conductive inorganic powdery or granular substances or the electrically conductive fibrous substances and/or corpuscles exceeds the amounts stated.

Any moulding method can be used in order to obtain the desired moulded products from a composition comprising the resin and the electrically conductive inorganic powdery or granular substances and the electrically conductive fibrous substances and/or corpuscles (hereinafter referred to as the electrically conductive fillers). For example, in the case of the above described thermoplastic resins, it is desirable that moulded products of the desired shapes be obtained by mixing the electrically conductive fillers with resin at a definite ratio, pelleting the resulting mixture in an extruder and then moulding by means of an injection-moulding machine. In addition, moulded products of the desired shapes can be obtained by extruding the hybrid composition into sheet-like substances by means of a mixing extruder and then moulding them into products of the desired shapes by vacuum moulding or pressure forming. In the case of the above described emulsion-type or latex-type resin, a slurry of the materials can be sprayed directly on the surface of a large-sized frame and then dried, or alternatively a hybrid composition can be mixed and then extruded into sheet-like substances, which are dried and then moulded into products of the desired shapes. In the case of thermosetting resin, known or conventional methods are used. The effects of the present invention can be heightened by reinforcing compounds such as SMC and BMC with hybrid reinforcement, simultaneously using the electrically conductive fillers and glass fibres.

It has been found that moulded products obtained according to the present invention can be superior in electromagnetic shielding property and rigidity to previously known products. These performances are evaluated in

the following manner. Although it is desirable that the electromagnetic shielding effect be measured in accordance with the method provided by FCC (Federal Communication Commission) of USA, it can also be evaluated by a convenient method described in for example "Engineering Materials", 29 (12) 31, 38. According to this method, an electric motor or sparks are used as the source of noises, and signals received by a dipole antenna are detected by means of a spectrum analyser or a field strength meter. However, a quasi-peak detecting method ought to be used. On the other hand, mechanical characteristics such as flexural modulus, tensile strength and heat-distortion temperature are measured and evaluated in accordance with JIS and ASTM for separate plastics materials.

Since resin compositions according to the present invention are superior in electromagnetic shielding, rigidity, and heat resistance they can be widely used for housing, inter alia, electronic instruments, communications instruments, medical instruments and measuring instruments, such as TV-games, electronic platemaking machines, electronic typewriters, electronic time-recorders, electronic bench calculators, electronic sewing machines, electronic registers, electronic ranges, personal computers, facsimile copying machines, printers, VTRs, plotters, word processors, display equipment and ultrasonic diagnostic equipment. They are effectively used especially for apparatus and instruments containing computers.

The present invention is described in the following illustrative Examples, which refer to preferred embodiments, to which the invention is not limited. Parts and percentages are by weight unless the contrary is stated. Comparative Examples are also included.

EXAMPLE 1, COMPARATIVE EXAMPLES 1 to 3

Nickel is deposited on the surface of powdery or granular phlogopite (Suzorite mica from Canada dealt with by Kuraray Co. Ltd.) having an average diameter of 90 μm and an average aspect ratio of 50 by an electroless plating method. The nickel content of the resulting metal-coated mica is 30% determined from the loss in weight after rinsing with nitric acid. Then 0.5% of α-aminopropyltriethoxysilane based on the mica, and the indicated amounts of the metal-coated powdery or granular mica and of metal fibres, are added to commercially available polypropylene resin pellets, which are used as matrix resin, in a Henschel mixer with stirring.

The metal fibres are of brass and have an average diameter of 60 µm and an average fibre length of 3 mm (the average aspect ratio is 50). The amount of metal-coated powdery or granular mica is 25 parts per 70 parts of the resin, the amount of metal fibre is 5 parts per 70 parts of the resin. Subsequently, the resulting mixture is melted and mixed at 250 °C in a uniaxial extruder to obtain pellets. The resulting pellets are moulded into test pieces by injection moulding and into sheet-like substances 3 mm thick by an extrusion moulding. The heat distortion temperature of this resin composition measured in accordance with ASTM D 648 (at a load of 18.6 kg/cm^2) is 124 °C and its flexural modulus measured in accordance with ASTM D 790 is 4.8×10^4 kg/cm^2. The sheet-like substances are analysed by a spectrum analyser using a motor as a source of noises in the same electromagnetic shielding effect-measuring apparatus as described in "Engineering Materials", 29 (12), 38. The shielding effect obtained is 30 db for a frequency of 10 MHz, 34 db for a frequency of 100 MHz and 39 db for a frequency of 1 GHz.

In Comparative Example 1, only the polypropylene of Example 1 is used. In Comparative Example 2 a moulded product obtained from a resin composition in which only the metal-coated mica (25%) is added to the polypropylene resin as in Example 1 is used. In Comparative Example 3, moulded products obtained from a resin composition in which only the brass fibres (5%) are added to the polypropylene resin as in Example 1. These materials are tested for physical properties in the same manner as in Example 1. It is found that the heat distortion temperatures of the moulded products are 58 °C, 110 °C and 65 °C in Comparative Examples 1, 2 and 3 respectively; the flexural moduli of the moulded products are 1.2×10^4 kg/cm^2, 4.0×10^4 kg/cm^2 and 4.8×10^4 kg/cm^2 in Comparative Examples 1, 2 and 3 respectively. The electromagnetic shielding effect of moulded products obtained from a resin composition of Comparative Example 2 is 18 db for a frequency of 10 MHz, 22 db for a frequency of 100 MHz and 28 db for a frequency of 1 GHz. On the contrary, the electromagnetic shielding effect of moulded products obtained for the resin compositions of Comparative Examples 1 and 3 is from 2 to 3 db for all frequencies, that is to say no perceptible effect is achieved. It is obvious from the above described results that a hybrid resin composition according to the present invention is superior to resin alone in rigidity, heat resistance

and electromagnetic shielding; is superior to a resin composition containing a small amount of metal fibres in heat resistance and electromagnetic shielding; and is superior to a resin composition containing only metal-coated mica in electromagnetic shielding.

EXAMPLE 2 and COMPARATIVE EXAMPLES 4 to 6

Copper is deposited on the surface of powdery or granular muscovite from India (an average diameter of 60 µm and an average aspect ratio of 32) by an electroless plating method. Two copper-coated powdery or granular micas, having metal contents of 35% and 13% respectively were obtained by selecting the concentration of an electroless metal ion solution and the plating time. High-vacuum aluminized glass fibres having an average diameter of 20 µm and an average fibre length of 2.5 mm (an average aspect ratio of 125) are used for electrically conductive fibrous substances. Then the following resin compositions were made up: (Example 2) a hybrid resin composition consisting of a commercially available polybutylene terephthalate matrix resin, 40% of the electrically conductive powdery or granular mica having a copper content of 35% and 3% of the high-vacuum aluminized glass fibres; Comparative Example 4 a hybrid resin composition consisting of a commercially available polybutylene terephthalate matrix resin, 7% of the electrically conductive powdery or granular mica having a copper-content of 13% and 3% of the high-vacuum aluminized glass fibres; (Comparative Example 5) a hybrid resin composition consisting of a commercially available polybutylene terephthalate matrix resin, 40% of the electrically conductive powdery or granular mica having a copper-content of 35% by weight and 25% of the high-vacuum aluminized glass fibres; and (Comparative Example 6) polybutylene terephthalate resin only.

Each of these resins is moulded into test pieces and sheet-like substances at 240 °C in the same manner as in Example 1, except that it was difficult to mix the hybrid resin composition of Comparative Example 5, so test pieces of the composition of this Comparative Example could not be obtained. The physical properties of the resulting moulded products are tested in the same manner as in Example 1. The heat distortion temperature of the moulded products obtained from the compositions of Example 2, Comparative Example 4 and Comparative Example 6 are 173 °C, 69 °C and 60 °C, respectively. The flexural modulus of the moulded products obtained from the compositions of Example 2, Comparative

Example 4 and Comparative Example 6 are 9.5×10^4 kg/cm^2, 3.2×10^4 kg/cm^2 and 2.5×10^4 kg/cm^2, respectively. The electromagnetic shielding effect of moulded products obtained from a hybrid resin composition of Example 2 is 31 db for a frequency of 10 MHz, 42 db for a frequency of 100 MHz and 46 db for a frequency of 1 GHz. The electromagnetic shielding effect of moulded products obtained from the composition of Comparative Example 4 is 2 to 5 db for all frequencies and that of moulded products obtained from polybutylene terephthalate resin alone is 2 to 3 db. It is obvious from the above described results that the electrical resistivity of the moulded products is reduced, whereby the electromagnetic shielding effect is reduced, when the electrically conductive flaky inorganic powdery or granular substances are added in small ratios, while it is difficult to mould a resin composition when the electrically conductive fibrous substances are added at ratios larger than that according to the present invention, that is to say a hybrid resin composition according to the present invention is superior in rigidity, mouldability and electromagnetic shielding effect.

EXAMPLE 3

Aluminium is deposited on the surface of powdery or granular phlogopite having an average diameter of 250 μm and an average aspect ratio of 65 by the high-vacuum metallizing method so that the resulting aluminized mica contains 40% of aluminium. 45 parts of the resulting aluminized powdery or granular mica and 15 parts of ketjenblack (powdery graphite) having an average diameter of 0.1 μm are added to 40 parts of a commercially available unsaturated polyester resin with stirring. Then the resulting mixture is mixed with a curing agent consisting of methyl ethyl ketone peroxide and cobalt naphthenate to prepare a paste. Glass mats are impregnated with the resulting paste, the paste-impregnated mats being piled up and cured at room temperature and further subjected to after-cure at 100 °C to obtain built-up FRP plates 5 mm thick. The electromagnetic shielding effect of the resulting FRP plates is 45 db for a frequency of 100 MHz. It is obvious from the test results of this Example that a hybrid resin composition according to the present invention is superior in an electromagnetic shielding effect.

EXAMPLE 4 and COMPARATIVE EXAMPLES 7 and 8

Nickel is deposited on the surface of powdery or granular phlogopite

(Suzorite mica from Canada sold by Kuraray Co. Ltd.) having an average diameter of 220 μm and an average aspect ratio of 60 by an electroless plating method. The nickel content of the resulting metal-coated mica is about 20% and the volume resistivity measured for an insulating cylindrical receptacle filled with said metal-coated mica at a load of 50 g/cm^2 by the double bridge method is 5.6×10^{-2} ohm·cm. The electrical resistivity of brass fibres having an average diameter of 60 μm and an average fibre length of 3 mm similarly measured is 2.5×10^{-2} ohm·cm. Then 30 parts of the nickel-coated mica and 10 parts of the brass fibres are mixed with 60 parts of an ABS resin, which is used as matrix resin. The resulting mixture is melted, mixed at 240 °C in a uniaxial extruder, extruded into strand-like substances and cut to obtain pellets. Subsequently, test pieces are obtained from the resulting pellets by injection moulding and sheet-like substances 3 mm thick are obtained from the resulting pellets by an extrusion moulding. These are the materials of Example 4.

In Comparative Example 7, 30 parts of aluminium flakes having an average diameter of 1 mm and an average thickness of 30 μm (volume resistivity of 7.4×10^{-4} ohm·cm) are used instead of the nickel-coated mica used in Example 4, and in Comparative Example 8, 30 parts of nickel powder having an average diameter of 3 μm (volume resistivity of 7×10^{-2} ohm·cm) are used instead of the nickel-coated mica used in Example 4 in compositions that are moulded in the same manner as in Example 4. However, the composition of Comparative Example 7 cannot be moulded since the nozzle was choked in an extrusion moulding process. Therefore, the composition of Comparative Example 7 is mixed in a Labo Plastomill manufactured by Toyo Seiki Co. Ltd. and then moulded into the desired shapes by means of a hot press to obtain test pieces. In Example 4, Comparative Example 7 and Comparative Example 8 the heat distortion temperature of the moulded products is 115 °C, 93 °C and 94 °C respectively; the flexural modulus of the moulded products is 9.8×10^4 kg/cm^2, $3.3. \times 10^4$ kg/cm^2 and 3.0×10^4 kg/cm^2 respectively, and the electromagnetic shielding effect of sheet-like substances 3 mm thick for an electromagnetic wave of 10 MHz is 40 db, 35 db and 10 db respectively. It is obvious from the above described results that a hybrid resin composition according to the present invention is superior in rigidity, heat resistance and electromagnetic shielding.

The mouldability is remarkably reduced so that metal pieces and metal fibres are deformed to show the uneven distribution in moulded products: as a result the superior electromagnetic shielding effect cannot be achieved in Comparative Example 7 in which flaky electrically conductive metal pieces are used instead of electrically conductive inorganic powdery or granular substances used as one of constituent elements in the present invention. Also in Comparative Example 8, in which metal particles but not metal flakes are used, metal fibres are slightly deformed, so that the superior electromagnetic shielding effect cannot be achieved. The differences between moulded products obtained from a hibrid resin composition of Example 4 and those obtained from a hybrid resin composition of Comparative Example 7 in the state of electrically conductive powdery or granular substances and metal fibres can be clearly understood from the photomicrographs shown in Figs. 4, 5 and 6.

EXAMPLE 5 and COMPARATIVE EXAMPLES 9 and 10

38 parts of nickel-coated mica obtained as in Example 4 and 2 parts of ketjenblack having an average diameter of 0.1 μm (volume resistivity of 1×10^{-1} ohm.cm), which is an electrically conductive carbon black, are added to 60 parts of ABS resin and the resulting composition is moulded in the same manner as in Example 4 to obtain test pieces (Example 5). A composition consisting of 97 parts of ABS resin and 3 parts of ketjenblack (Comparative Example 9) and a composition (Comparative Example 10) consisting of 60 parts of ABS resin, 38 parts of the aluminium flakes used in Comparative Example 7 and 2 parts of ketjenblack are moulded in the same manner as in Example 5. However, it is difficult to mould a composition containing aluminium flakes (Comparative Example 10) by extrusion. Consequently, moulded products were obtained by the hot pressing method as in Comparative Example 7. The heat distortion temperatures of moulded products obtained from the compositions of Example 5, Comparative Example 9 and Comparative Example 10 are 113 °C, 93 °C and 95 °C respectively, their flexural moduli are 12.5×10^4 kg/cm^2, 2.8×10^4 kg/cm^2 and 3.4×10^4 kg/cm^2, respectively, and the electromagnetic shielding effect of sheet-like materials 3 mm thick obtained from these compositions for the frequency of 100 MHz is 45 db, 2 to 3 db and 36 db respectively.

It is clear from the above described results that a hybrid resin composition according to the present invention is superior in rigidity, heat

resistance and electromagnetic shielding property. Although a composition of Comparative Example 9 contains ketjenblack in the almost same ratio as in Example 5, moulded products obtained from it show hardly any electromagnetic shielding effect. That is to say, the superior electromagnetic shielding effect cannot be achieved unless ketjenblack is added together with electrically conductive inorganic powdery or granular substances, which are one of the constituent elements in the present invention. The compositions of Comparative Example 10 is inferior to that of Comparative Example 7 in mouldability. In addition, the composition of Comparative Example 10 shows the remarkable maldistribution of metal pieces and is therefore remarkably fragile.

CLAIMS

1. A hybrid resin composition comprising (A) 10 to 50 parts by weight of electrically conductive inorganic powdery or granular substances, which are obtained by coating the surface of flaky nonmetallic inorganic powdery or granular substances with electrically conductive materials having volume resistivity of 1 ohm•cm or less; (B) 1 to 20 parts by weight of an electrically conductive fibrous substance and/or electrically conductive corpuscles having a volume resistivity of 1 ohm•cm or less, and (C) 30 to 80 parts by weight of a resin.

2. A composition as claimed in Claim 1, in which the flaky nonmetallic inorganic powdery or granular substances are powdery or granular substances of which the surface is coated with 0.2 to 1 times its weight of the electrically conductive materials.

3. A composition as claimed in Claim 1 or 2, in which the flaky nonmetallic inorganic powdery or granular substances have an average aspect ratio (a ratio of diameter to thickness) of 10 or more.

4. A composition as claimed in any preceding claim, in which the flaky nonmetallic inorganic powdery or granular substances are natural or artificial minerals belonging to the mica, clintonite or chlorite group.

5. A composition as claimed in any preceding claim in which the electrically conductive materials are at least one of silver, aluminium, copper, nickel, chromium, titanium, tin, antimony, zinc, gold, platinum, iron, alloys containing those metals and graphite.

6. A composition as claimed in any preceding claim in which the electrically conductive fibrous substances have an average aspect ratio of 10 or more.

7. A composition as claimed in any preceding claim in which the electrically conductive fibrous substances comprise metal fibres, organic or inorganic fibres coated with metals, carbon fibres, graphite fibres and/or organic fibres containing metal or carbon corpuscles.

8. A composition as claimed in any preceding claim in which the electrically conductive corpuscles are corpuscles of at least one of the materials listed in Claim 5.

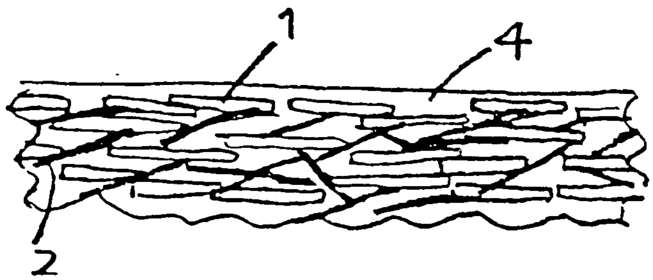


FIG.1

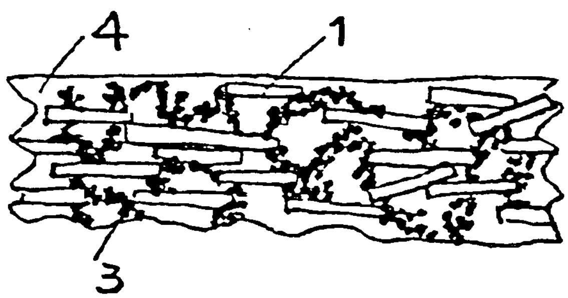


FIG.2

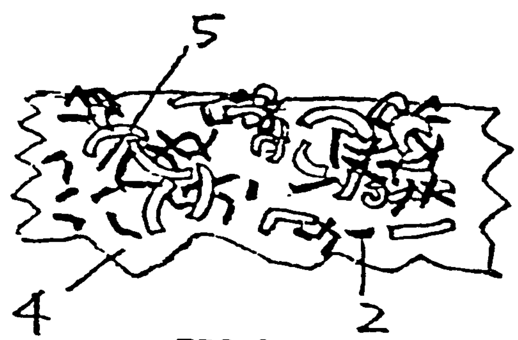


FIG.3

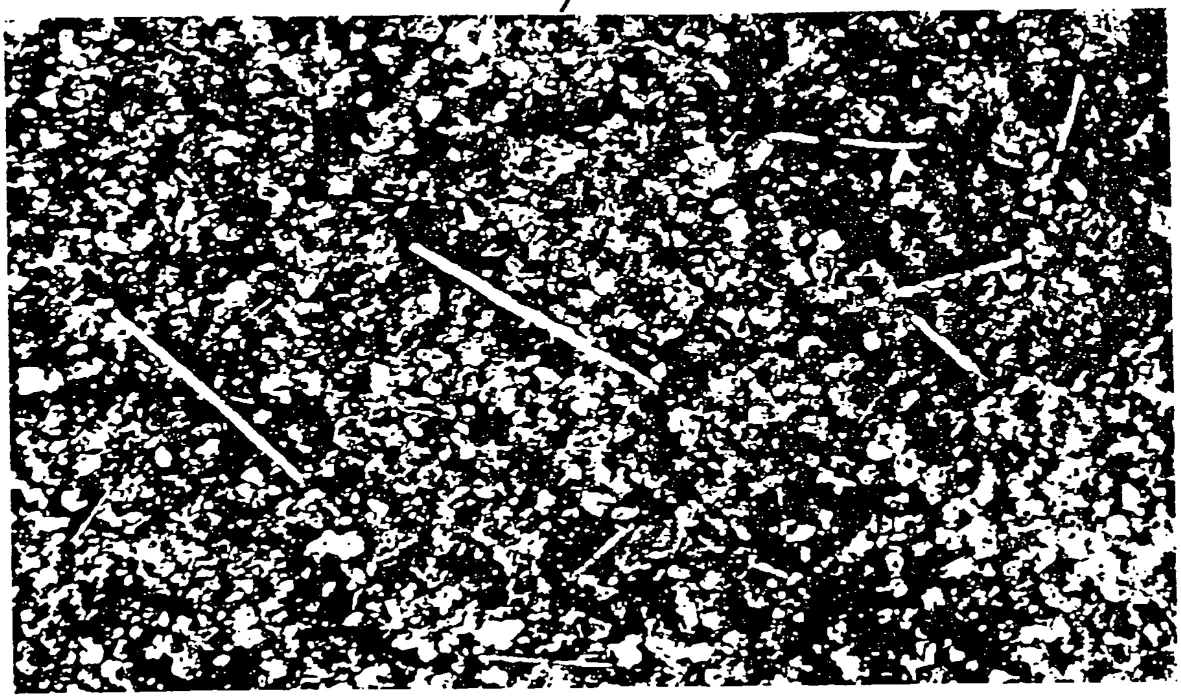


FIG.4

0 1 2

mm

FIG.5

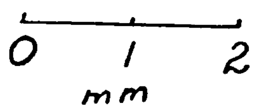
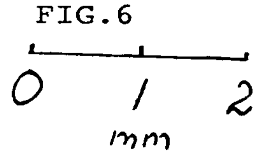


FIG.6



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EUROPEAN SEARCH REPORT

Application number

EP 84 30 1088

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	DE-A-3 135 921 (POTTERS) * Claims 1-37 *	1,5	H 01 B 1/22 H 01 B 1/24

			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			H 01 B 1/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-05-1984	DROUOT M.C.

CATEGORY OF CITED DOCUMENTS

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